

- (c) flowing H₂/Ar gas within said vessel and increasing the pressure within said vessel;
- (d) increasing the temperature of said prepared substrate; and
- (e) changing said H₂/Ar gas to ethylene gas such that said ethylene gas flows within said vessel.

23. (amended) The method as recited in claim 13, wherein said conductive substrate is selected from the group consisting of titanium, titanium carbide, vanadium, tantalum, and combinations thereof.

Pursuant to the requirements of Rule 1.121(c), a copy of the amended claims is attached as a separate paper showing the foregoing changes with added matter underlined and deleted matter [in brackets].

SUMMARY OF AMENDMENTS

An additional drawing (attached as FIG. 1) has been provided to provide consistency with the parent case. Numerous minor changes have been made to the description portion of the Specification to ensure consistency with (1) the parent case, (2) the labels and reference characters associated with the attached replacement drawings, and (3) to ensure the consistent and clear use of "conductive" and "prepared" substrates throughout the Specification. The Title was changed to ensure consistency with the claim scope that changed as a result of the restriction requirement in the parent case. The cross reference to related applications section was added to provide proper reference to the parent case. Claim 13 was reworded to be more clear and to incorporate the scope of cancelled claim 22. Claim 22 was cancelled as claim 13 was amended to incorporate the limitations of Claim 22. Claim 23 was amended to correct its dependency because of the cancellation of its base claim, claim 22. Claim 25 was cancelled due to its redundancy with claim 16. No new matter has been added in any of the foregoing amendments. As the Applicant argued persuasively in the parent case, the originally-filed application states:

- (1) "the substrate is a conductive substrate coated with a growth catalyst"
(page 3, lines 27-28)

whereby the present invention provides a method that:

- (2) "includes the steps of depositing a growth catalyst onto the conductive

- substrate as a prepared substrate" (page 4, lines 2-4) and
- (3) "includes the steps of depositing a growth catalyst onto the substrate to form a prepared substrate" (page 5, lines 19-20)

Again, as the Applicant argued persuasively in the parent case, there is only one logical and consistent interpretation of the "the substrate" in (3) above in view of (1) and (2). That is, "the substrate" in (3) must be "the conductive substrate." Using the same logic and to be consistent, "the substrate" in (1) must therefore be "the prepared substrate."

Thus, the amendment changing the above statements to (where underlined matter is inserted and bracketed matter deleted):

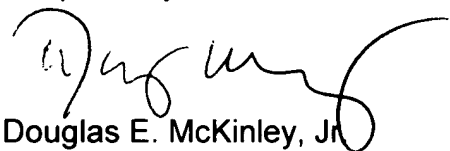
- (1') "the prepared substrate is a conductive substrate coated with a growth catalyst"
- (2') "includes the steps of depositing a growth catalyst onto [the] a conductive substrate [as a] to form the prepared substrate"
- (3') "includes the steps of depositing a growth catalyst 150 onto [the] a conductive substrate 160 to form [a] the prepared substrate 120"

does not introduce new matter since the amendment is based on a logical conclusion using information in the originally-filed Specification.

CLOSURE

Applicant has made an earnest attempt to place the above-referenced application in condition for allowance and action toward that end is respectfully requested. Should the Examiner have any further observations or comments, he is invited to contact the undersigned for resolution.

Respectfully submitted,



Douglas E. McKinley, Jr.
Reg. No. 40,280

McKinley Law Office
PO Box 202
Richland, WA 99352
Voice (509) 628-0809

Fax (509) 628-2307

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:) Art Unit:
Y Gao and J Liu) Examiner:
Serial No: 09/996,523) Paper No. 2
Filed: 06/14/99) Our Ref. No: E-1743DIV
For: CARBON NANOTUBES ON A SUBSTRATE AND METHOD OF MAKING) Date: JAN 6, 2001

Version of amended specification (other than claims) to show changes made pursuant to Rule 1.121(b) with added matter underlined and deleted matter [in brackets].

METHOD OF MAKING CARBON NANOTUBES ON A SUBSTRATE
[CARBON NANOTUBES ON A SUBSTRATE AND METHOD OF MAKING]

CROSS REFERENCE TO RELATED APPLICATIONS

This Application is a divisional of US Ser. No. 09/333,876, filed 06/14/99, now US Patent _____.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates generally to the synthesis of carbon nanotubes on substrates. More specifically, the invention relates to dense arrays of well-aligned

carbon nanotubes filled with conductive filler synthesized on conductive substrates and a method for making these carbon nanotubes.

BACKGROUND OF THE INVENTION

Carbon nanotubes constitute a new class of materials with a broad range of potential applications. Their unique properties make carbon nanotubes ideal candidates for novel application in areas such as vacuum microelectronics, flat panel displays, scanning probes and sensors, field emission devices and nanoelectronics.

A wide range of techniques has been used to prepare carbon nanotubes. For example, carbon nanotubes can now be produced in high yield and with reasonable quality as reported by C. Journet et al., *Nature* 388, 756 (1997), using arc discharge, by A. Thess et al., *Science* 273, 483 (1996), using laser ablation, and by R. T. Baker, *Carbon* 27, 315 (1989), using thermal decomposition of hydrocarbons.

Alignment of carbon nanotubes is particularly important for their use in applications such as flat panel displays. Ajayan et al., *Science* 265, 1212 (1994) report manufacturing a composite with carbon nanotubes randomly dispersed inside a polymer resin matrix and found that slicing the composite caused partial alignment of the nanotubes on the cut surface. De Heer et al., *Science* 268, 845 (1995) fabricated partially aligned nanotube films by drawing a nanotube suspension through a micropore filter.

More recently, well-aligned carbon nanotube arrays have been synthesized on solid substrates. W. Z. Li et al., *Science* 274, 1701 (1996), report well-aligned carbon nanotube arrays synthesized by thermal decomposition of acetylene gas in nitrogen on porous silica containing iron nanoparticles, and Z. F. Ren et al., *Science* 282, 1105 (1998), report well-aligned carbon nanotube arrays synthesized by hot-filament plasma-enhanced thermal decomposition of acetylene gas on nickel-coated glass. All of these preparations however, result in isolated carbon nanotubes on substrates where all the nanotubes are separated by distances on the order of 100 nanometers within the arrays. Disadvantages of these separations between the carbon nanotubes include decreased nanotube capacity on the substrate and a decreased ability to maintain

alignment as the nanotubes grow longer.

Although hollow carbon nanotubes have substantial utility, it is recognized that filling the hollow core of carbon nanotubes with materials having useful physical, chemical, and electronic properties significantly broadens the range of potential applications for carbon nanotubes. Early attempts to fill carbon nanotubes were based on electric arc or laser ablation methods using metal/carbon composites as reported for example by Zhang et al., *Science* 281, 973 (1998), or on capillary-force infiltration of open-ended nanotubes as reported by Ugarte et al., *Science* 274, 1897 (1996). In addition, Dia et al., *Nature* 375, 769 (1995), reported an attempt to fill carbon nanotubes resulting in the reaction of the carbon nanotubes with titanium oxide (TiO) which converted all the nanotubes into titanium carbide (TiC) nanorods. In these and other prior experiments the carbon nanotubes were found to be only partially filled to a level of approximately 10%. The disadvantage of having carbon nanotubes that can only be partially filled is a decrease in the benefit sought to be gained through the useful properties of the materials filling the nanotube cores.

In view of the current and potential applications for carbon nanotubes, there remains a need in carbon nanotube technology for a method of synthesizing dense arrays of well-aligned carbon nanotubes on conductive substrates where the nanotubes are simultaneously and completely filled with conductive materials.

SUMMARY OF THE INVENTION

The present invention includes carbon nanotubes whose hollow cores are 100% filled with conductive filler. The carbon nanotubes are in uniform arrays on a prepared [conductive] substrate and are well-aligned and can be densely packed. The uniformity of the carbon nanotube arrays is indicated by the uniform length and diameter of the carbon nanotubes, both which vary from nanotube to nanotube on a given array by no more than about 5%. The alignment of the carbon nanotubes is indicated by the perpendicular growth of the nanotubes from the [substrates] prepared substrate which is achieved in part by the simultaneous growth of the conductive filler within the hollow core of the nanotube and the densely packed growth of the nanotubes. The present

invention provides a densely packed carbon nanotube growth where each nanotube is in contact with at least one nearest-neighbor nanotube. The prepared substrate is a conductive substrate coated with a growth catalyst, and the conductive filler can be single crystals of carbide formed by a solid state reaction between the conductive substrate material and the growth catalyst.

The present invention further provides a method for making the filled carbon nanotubes on [the conductive] prepared substrates. The method includes the steps of depositing a growth catalyst onto [the conductive substrate as a] a conductive substrate to form the prepared substrate, creating a vacuum within a vessel which contains the prepared substrate, flowing H₂/inert (e.g. Ar) gas within the vessel to increase and maintain the pressure within the vessel, increasing the temperature of the prepared substrate, and changing the H₂/Ar gas to ethylene gas such that the ethylene gas flows within the vessel. Additionally, varying the density and separation of the catalyst particles on the conductive substrate can be used to control the diameter of the nanotubes.

It is an object of the present invention to provide a method for the synthesis of dense arrays of well-aligned carbon nanotubes on [conductive] prepared substrates [prepared with a growth catalyst] where each carbon nanotube is simultaneously and completely filled with a conductive filler.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of an array of a plurality of carbon nanotubes.

FIG. [1a] 2a is a photograph of a scanning electron microscopy micrograph illustrating the dense and well-aligned morphology of the carbon nanotube [films] array.

FIG. [1b] 2b is a photograph of a scanning electron microscopy micrograph

illustrating the structure of the carbon nanotubes.

FIG. [1c] 2c is a photograph of a scanning electron microscopy micrograph illustrating a tilted carbon nanotube revealing the nanowire-like structure of the conductive filler [a nanowire] enclosed within.

FIG. [2a] 3a is a photograph of a cross-sectional transmission electron microscopy illustrating the nature of the conductive fillers [(nanowires)] filling the core of carbon nanotubes.

FIG. [2b] 3b is an energy-dispersive x-ray spectra illustrating that the core of the conductive filler [nanowire] is comprised of both titanium and carbon.

FIG. [2c] 3c is a photograph of a high resolution transmission electron microscopy illustrating that the carbon walls are disordered graphite.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

As shown in **FIG. 1**, [T]the present invention is an array of a plurality of carbon nanotubes 100 where each carbon nanotube 110 [nanotube] is attached [to a substrate and extends from the substrate] to, and extends from, a prepared substrate 120 and has a closed outer wall 130 defining a hollow core that is simultaneously filled more than 10% with a conductive filler 140 while the carbon nanotube 110 is formed [grows].

The present invention further provides a method for making this array of carbon nanotubes which includes the steps of depositing a growth catalyst 150 onto a conductive substrate 160 [onto the substrate] to form [a] the prepared substrate 120, creating a vacuum within a vessel which contains the prepared substrate, flowing H₂/inert (e.g. Ar) gas within the vessel and increasing the pressure within the vessel, increasing the temperature of the prepared substrate, and changing the H₂/Ar gas to ethylene gas such that the ethylene gas flows within the vessel.

The arrays of the carbon nanotubes filled with conductive filler are fabricated by first depositing a thin layer of growth catalyst 150 onto the conductive substrate 160 [onto a substrate]. Depositing the growth catalyst is preferably by electron beam evaporation, and preferably results in a thin layer on the conductive substrate which is about 1 to 30 nanometers in thickness. The conductive substrate is

an electrically conductive substrate, preferably made of metals including but not limited to transition elements appearing in groups IIIB, IVB, VIB, VIIB, VIII, and IB of the periodic table. Preferred metals are titanium, vanadium, tantalum, and combinations thereof. Non-metals such as carbides may also be used for the conductive substrate, for example, titanium carbide. The growth catalyst is preferably iron, but may also be iron oxide and combinations thereof.

After the conductive substrate is prepared with the growth catalyst coating, the vessel which contains the prepared substrate is evacuated to a first pressure below 2 torr. The vessel is preferably a quartz reactor placed within a tube furnace. The pressure within the vessel is then increased to a second pressure within the range from about 200 torr to about 400 torr by flowing H₂/inert (e.g. Ar) gas within the vessel. After the pressure stabilizes within the vessel, the prepared substrate is heated using the tube furnace. Once the prepared substrate temperature reaches the growth temperature, which can range from about 650°C to about 800°C, but which is preferably from about 700°C to 775 °C, the H₂/Ar flow is stopped and ethylene gas, preferably but not necessarily with a purity of about 99.5%, is introduced into the reactor. A preferable introduction flow rate of 200 cm³/min. Typical growth periods range from about 10 minutes to 3 hours.

The heat treatment of the prepared substrate can be controlled to vary the density and separation of catalyst particles on the prepared substrate. A higher heat results in more coalescing of the catalyst particles, and thus, fewer and larger catalyst sites, which results in separation distances between these sites on the prepared substrate. The density of the catalyst sites controls the diameter of the carbon nanotubes with a higher density resulting in a greater diameter carbon nanotube. As the ethylene gas flows, it decomposes as a carbon source and diffuses into the catalyst particles causing precipitation and growth of the carbon nanotubes. At the same time, the conductive substrate material diffuses into the catalyst particles resulting in the growth of a carbide core (conductive filler) within the hollow carbon nanotubes. The carbide core within the carbon nanotubes is a conductive filler preferably made up of carbon and titanium. However, the conductive filler may also be made up of carbon and whichever metal makes up the conductive substrate, which includes but is not

limited to transition elements appearing in groups IIIB, IVB, VIB, VIIB, VIII, and IB of the periodic table. Preferred metals are titanium, vanadium, tantalum, and combinations thereof. The hollow core of each carbon nanotube is filled with the conductive filler to a point which is greater than 10% full, but which is preferably greater than 50% full, and which is more preferably greater than 75% full, and which is most preferably about 100% full, where "about 100%" means 100%, plus or minus 5%.

The carbon nanotubes have lengths ranging from about 1 to 2 μm , varying no more than about 5%, which provides uniform lengths. The carbon nanotubes also have uniform diameters such that their diameters vary no more than about 5%. The outside nanotube diameter ranges from less than 40 to about 400 nm and the inside nanotube diameter ranges from about 10 to about 100 nm. The diameters of the carbon nanotubes and filled cores can be controlled by varying the thickness of the catalyst (iron) layer. In general, the thicker the iron catalyst layer, the bigger the tube diameter. However, when the tube diameter is less than 40 nm, the carbon nanotubes are curved and only partially filled.

EXAMPLE 1

A number of conductive substrates were selected to investigate their effects on the formation of the filled carbon nanotubes. The formation of the filled nanotubes depends on the solubility of the iron (the catalyst) in the conductive substrate and the free energy of formation for the respective carbide phase. The conductive substrate materials [substrates] selected included tantalum, silicon, and molybdenum. All of these materials can form stable carbides. Carbon nanotubes were deposited on the prepared substrates under the same growth conditions used for growth of carbon nanotubes using [on] titanium conductive substrates. While dense arrays of filled carbon nanotubes were observed on tantalum conductive substrates similar to those shown in FIG. 2a [1a], only curved hollow carbon nanotubes were formed on silicon conductive substrates. No carbon nanotubes were observed on molybdenum conductive substrates. For molybdenum conductive substrates, X-ray photoelectron spectrometry and backscattering electron SEM indicated formation of Fe-Mo solid solutions in the surface region of the prepared substrates. The high solubility of Fe in Mo depleted the catalytic material required to grow the carbon nanotubes. For silicon

conductive substrates, the driving force to form SiC is much lower than that for the formation of either TiC or TaC. The free energy of formation of these carbides is on the order of -43 kcal/mol for TiC, -35 kcal/mol for TaC, and -15 kcal/mol for SiC. Although carbon nanotubes are formed on prepared substrates using silicon conductive substrates [silicon], the growth rate of SiC is very low compared to that of TiC or TaC, resulting in hollow carbon nanotubes. These tubes tend to be tilted or curved.

The carbon nanotubes of the present invention are examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). **FIG. 2a [1a]** reveals the dense, well-aligned morphology of the carbon nanotube array [films]. The SEM images were recorded using 70% secondary electron signals and 30% back scattering electron signals. The intensity is therefore proportional to the atomic number of the elements that comprise the material. A magnified SEM image (**FIG. 2b [1b]**) shows that the structure of the carbon nanotubes of the present invention is different from that of oriented carbon nanotubes previously reported. First, the carbon tubes are densely packed, rather than well separated as with prior reported carbon nanotubes. Secondly, the tube tips as shown in **FIG.'s 2a, 2b, & 2c [1a, 1b, & 1c]**, appear brighter at the center of the carbon nanotubes, indicating that the cores of the carbon nanotubes are filled with a material having elements of higher atomic number than carbon.

Most of the carbon nanotubes filled with conductive filler of the present invention in **FIG. 2a [1a]** have similar length and are approximately perpendicular to the prepared substrate surface, although in a few cases the conductive filler is tilted and extended above the [film] surface. A SEM image (**FIG. 2c [1c]**) of a tilted nanotube reveals a structure of conductive filler enclosed by carbon. The filled material has a large head near the tube tip, and its diameter is about one quarter of the carbon nanotube diameter. Further evidence of filled cores and carbon caps is provided by the cross-sectional TEM image in **FIG. 3a [2a]** and energy-dispersive x-ray (EDX) spectra illustrated in **FIG. 3b [2a]**. The cross-sectional TEM image in **FIG. 3a [2a]** shows that individual conductive filler grows continuously from the bottom to the top of the carbon nanotubes [films]. The filled nature of the carbon nanotubes can be clearly seen by the distinct contrast between the filled core and carbon wall. The cross-sectional TEM

image in **FIG. 3a [2a]** reveals that the cores have a large head near the tube tip, in agreement with the SEM image (**FIG. 2c [1c]**). The core diameter in the cross-sectional TEM image in **FIG. 3a [2a]** appears slightly smaller than that observed in the SEM image (**FIG. 2c [1c]**), presumably due to the off-center cut of the TEM specimen. EDX analysis revealed that the walls and caps of the conductive fillers are carbon. A high-resolution TEM image (**FIG. 3a [2c]**) reveals that the carbon walls are disordered graphite.

EDX analysis of the carbon nanotube and conductive filler of the present invention also indicates that the core of the conductive filler is comprised of titanium and carbon except for the region near the prepared substrate where iron was found. Electron diffraction patterns obtained from the cores reveal that the cores are cubic TiC. The convergent beam electron diffraction pattern (inset in **FIG. 3a [2a]**) recorded along the $\langle 001 \rangle$ zone axis parallel to the electron beam exhibits a lattice spacing (~ 0.43 nm) and four-fold symmetry corresponding to the (100) planes of cubic TiC. In addition, the electron diffraction patterns reveal that the TiC cores are single crystals. In the high-resolution TEM image (**FIG. 3c [2c]**), the interface between the graphite wall and TiC core is abrupt and free of any intermediate phase. The magnified images show well-ordered lattice fringes of the TiC core (right inset of **FIG. 3c [2c]**) and disordered lattice fringes of the graphite wall (left inset of **FIG. 3c [2c]**). It should be pointed out that this is the first time that carbon nanotubes are completely filled with metallic TiC cores.

Moreover, all TiC cores show a big head near the tube tip (**FIG. 2c [1c]** and **3a [2a]**), indicating that the initial growth of the TiC cores is faster. This may be due to an initially high concentration of titanium dissolved in the iron particle during heating to the growth temperature (2.7 to 3 hours) before introducing ethylene gas into the reactor. After the initial growth, the dissolution and precipitation process reaches an equilibrium condition under which the consumed rate of titanium for the precipitation of TiC is approximately equal to the mass transfer rate of titanium into the iron particle, resulting in uniform core diameters. Carbon diffusion is not the limiting step in the formation of TiC because interstitial diffusion of carbon in iron is much faster than substitutional diffusion of titanium in iron.

Therefore it can be concluded that growth of oriented and filled carbon

nanotubes requires stable catalytic particles and low free energy of formation of a reaction product in the core.

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

Version of amended claims to show changes made pursuant to Rule 1.121(c) with added matter underlined and deleted matter [in brackets].

13. (amended) A method for synthesizing an array of a plurality of carbon nanotubes, each of said carbon nanotubes having a first end attached to a conductive substrate, and a second end extending from said conductive substrate, each of said carbon nanotubes having a closed outer wall defining a core that is hollow, wherein said core is filled more than 10% with a conductive filler, comprising the steps of:

- (a) depositing a growth catalyst onto said conductive substrate forming a prepared substrate;
- (b) creating a vacuum within a vessel containing said prepared substrate;
- (c) flowing H₂/Ar gas within said vessel and increasing the pressure within said vessel;
- (d) increasing the temperature of said prepared substrate; and
- (e) changing said H₂/Ar gas to ethylene gas such that said ethylene gas flows within said vessel.

23. (amended) The method as recited in claim [22] 13, wherein said conductive substrate is selected from the group consisting of titanium, titanium carbide, vanadium, tantalum, and combinations thereof.

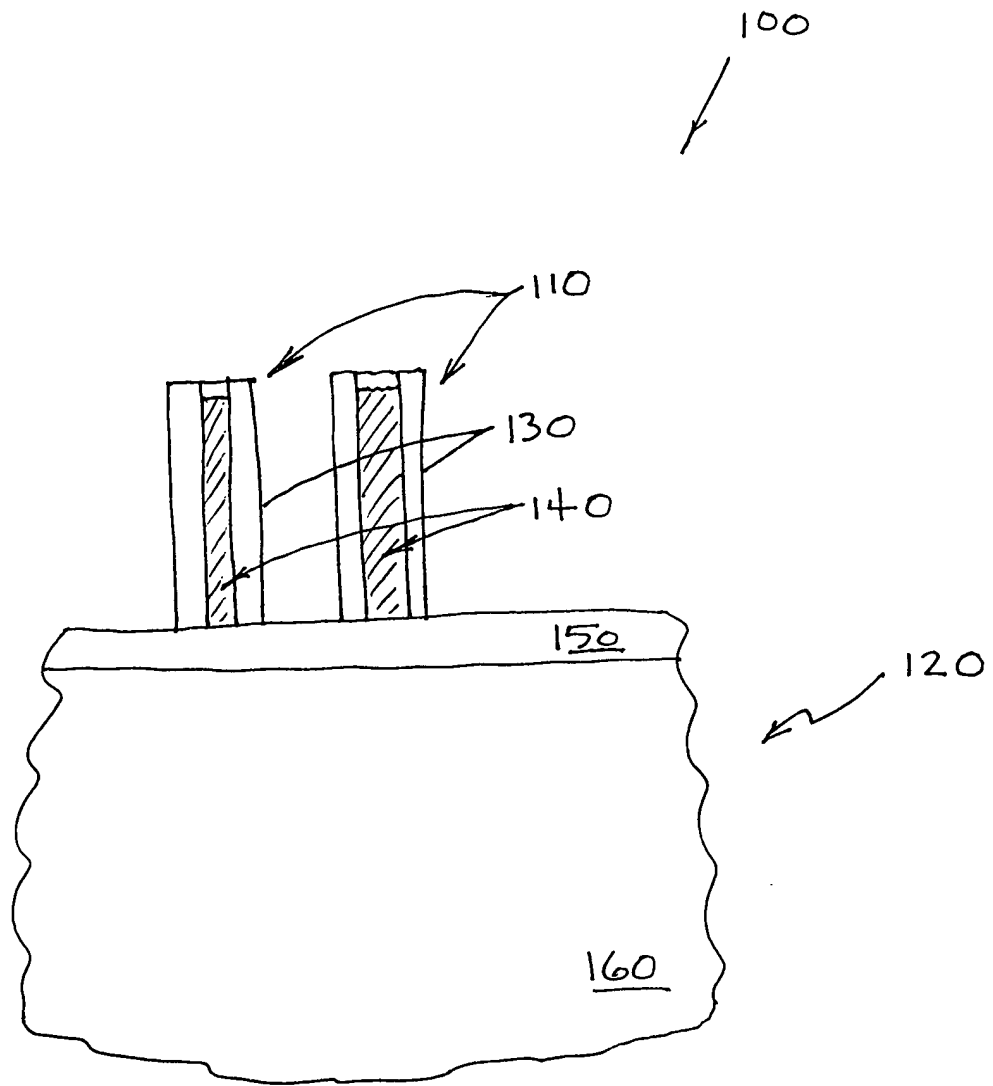


FIG. 1